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THE EFFECTS OF RADIATION ON  
NICKEL-CADMIUM BATTERY ELECTRODES. I

Final Report

1 June - 31 December 1963

Prepared for Jet Propulsion Laboratory

Under Contract No. 950514

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ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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By

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A DIVISION OF NORTH AMERICAN AVIATION, INC.  
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## SUMMARY

The effect of various types of radiation on the electrochemical and physical characteristics of nickel and cadmium electrodes was studied. The investigation for the most part employed electrodes in the flooded condition. The two principal effects of gamma irradiation were to cause material to be lost from the electrodes and to cause a buildup in gas pressure in sealed cells. In addition, a 10 mv decrease in cell voltage was observed in one experiment after a dosage of  $8.7 \times 10^7$  rads ( $H_2O$ ), and a decrease in capacity of the cadmium electrode by possibly as much as 25% was found after a dosage of  $3 \times 10^8$  rads ( $H_2O$ ).

The amount of material lost from the electrodes was found to increase with increasing total gamma dose. Also, the rate of material loss increased with increasing dose rate. The initiation of material loss, as determined by visual clouding of the electrolyte, occurred at about  $1.4 \times 10^6$  rads ( $H_2O$ ) for dose rates in the range of  $10^5$  to  $10^6$  rads ( $H_2O$ )/hour. The largest electrode material loss observed was about 77 mg after an irradiation of  $3 \times 10^8$  rads ( $H_2O$ ).

The material loss (sloughing) phenomenon was also observed in irradiations with electrons. The amounts lost with respect to total dose and dose rate were approximately consistent with the gamma irradiation results. Neutron irradiation results were inconclusive due to the low dose rate available.

The dislodged material showed cadmium to nickel ratios of 3:1 and greater, with the ratio decreasing with increased total irradiation dose. Individual electrode irradiations and complete commercial cell irradiations both indicated that this sloughed material was primarily being removed from the nickel electrode. Mechanisms based on radiolysis of the electrolyte are

suggested for this material loss. The effect of radiation on the electrolyte is to produce hydrogen peroxide and, to a lesser extent, hydrogen. Some evidence has been obtained to suggest that the hydrogen peroxide, either through chemical attack or through the mechanical effect associated with its decomposition to oxygen gas at the electrodes, may be one of the principal contributors to the material loss.

The pressure buildup in the cells is probably due principally to oxygen generated through the radiolytic and catalytic decomposition of hydrogen peroxide. The kinetics of the radiolysis in strong KOH are not known but extrapolation of data obtained in dilute base gave reasonable agreement with our data.



## I. INTRODUCTION

Batteries represent the source of secondary power on almost all space vehicles. In any orbit these vehicles and thus the batteries are subjected to various types of radiation from cosmic rays or the Van Allen belts. Future missions may incorporate nuclear reactors as the primary power source in the vehicle with batteries acting as the secondary power for standby and peak power intervals. The batteries may thus be in high radiation fields in this application. To study the effects of high radiation fields on these batteries, the nickel-cadmium system was chosen from the current types of rechargeable systems being used.

Previous studies<sup>1,2</sup> of nickel-cadmium batteries in radiation fields have been limited to an examination of the voltage and capacity before and after irradiation of the whole battery. No change in these parameters was observed. This present report describes a study of the behavior of individual electrodes in a radiation field and presents information on (a) the loss of material from the electrodes, (b) the effect of radiolytic decomposition of the electrolyte, and (c) some electrochemical changes which were observed.

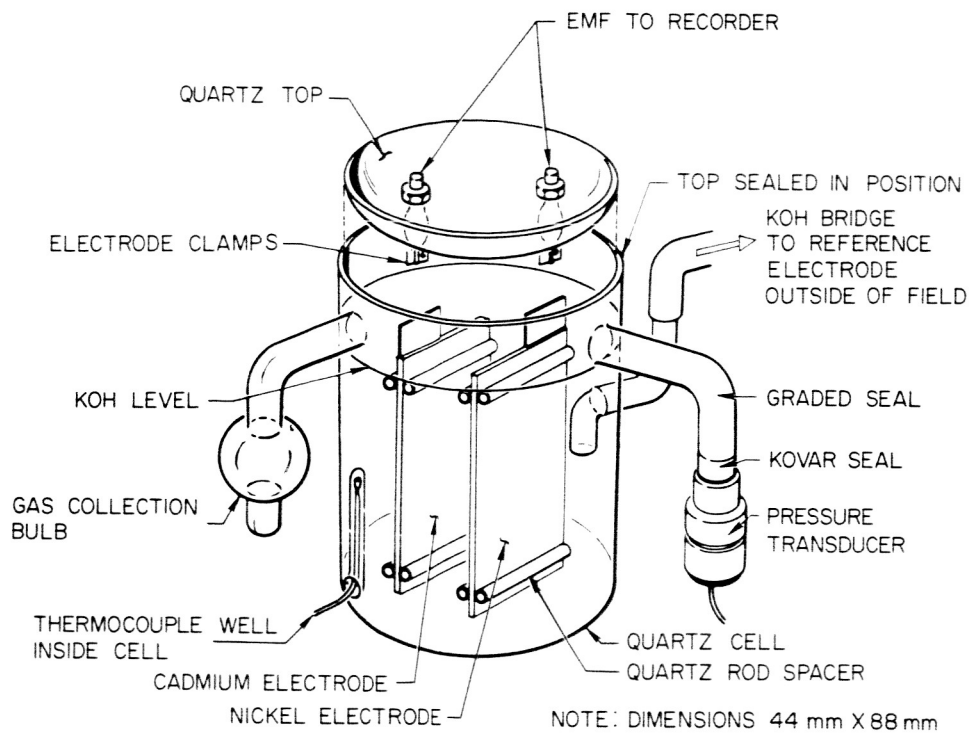
## II. EXPERIMENTAL PROGRAM

### A. MATERIALS AND EQUIPMENT

A diagram of the type of cell used for the initial experiments is shown in Figure 1. Individual electrodes were placed in holders so that electrode spacing is a constant for all runs. The cell and holders were of quartz which was employed because of its resistance to strong alkali solutions and to radiation. The experimental cell contains provision for a salt bridge to a reference Hg/HgO electrode outside the radiation field. The cell also contains a small bulb for collection of gases formed during irradiation. Connected to the cell inside the radiation field was a pressure transducer of the diaphragm type, sensitive to 0.1 psi.

Gulton Industries' nickel-cadmium type 10VO-8 flat plate cells were chosen for this study, mainly because of the ease in separating the individual electrodes for use in our test cells. Upon receipt, these commercial cells were charged according to the manufacturer's specifications, i.e., 0.060 amps for 17 hours. The physical size of these electrodes is 4.2 x 3.8 cms. The cells were disassembled and two of the three cadmium electrodes and the two nickel electrodes were then used to make two of our laboratory cells.

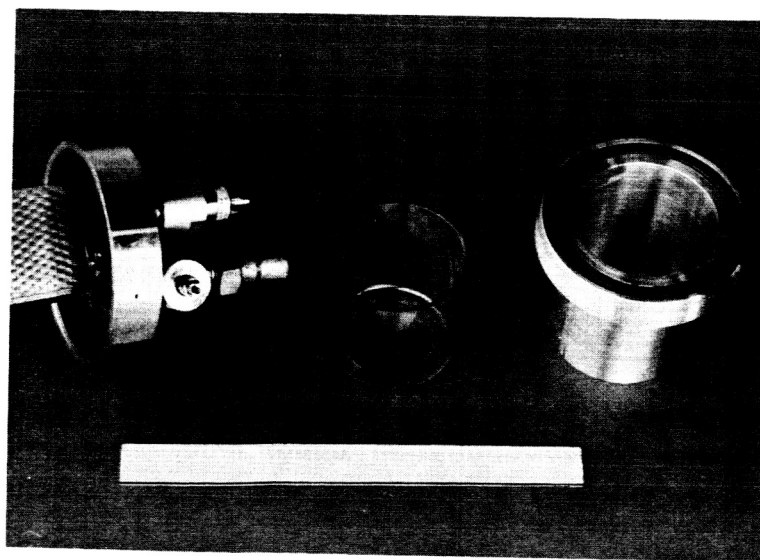
The laboratory cells were then discharged at 0.20 amps to the break in the discharge curve. To insure 100% charge of the cells they were charged for two and one half hours at 0.20 amps which is equivalent to 25% overcharge. Using the same current they were then discharged to 75% of full charge. This procedure was used for all cells. The cells were then cycled between 75% and 70% of charge for a period of 24 hours before irradiation treatment.



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Figure 1. Quartz Cell for Irradiations



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Figure 2. Stainless Steel Cell with Quartz Liner for Irradiations

A later cell design is shown in Figure 2. This stainless steel cell has a quartz liner to contain the electrodes and electrolyte. The reference electrode had to be incorporated inside the cell in this design. This type of cell was introduced to prevent the gas leakage encountered in the quartz cell design. Cells of similar physical dimensions to the cell of Figure 1 but made of lucite were used for electrochemical studies outside of the radiation fields.

The electrical circuit shown in Figure 3 was used to produce the cycling regime and to measure electrochemical effects during irradiation. The recorder was a Minneapolis-Honeywell Universal 5 mv instrument with  $\pm 50$  mv suppression. The constant current-constant voltage source was a Harrison Lab Model #855, the timer was Kelelet Model K213 and the multiscan timer was assembled from an Industrial Timer Kit #MCK. A solion device model #SV100 from Self Organizing Systems was used to give a state of charge indication. Two completely portable electrical power and recording systems were made for convenience in taking data.

## B. RADIATION SOURCES

### 1. Co-60 Gamma Sources

Two Co-60 gamma sources were used in this investigation. Source I gave a dosage of  $8 \times 10^4$  rads ( $H_2O$ ) per hour\* at the position of the cell in the source.

Source II is rated at  $1.4 \times 10^6$  rads ( $H_2O$ ) per hour. This source was used for most of the runs. A picture of it and one of the consoles is shown in Figure 4. The cell is placed in a 3" dia. x 5" deep well. Leads

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\*It is assumed for this work that the energy absorption of the electrochemical cell system is that of water.

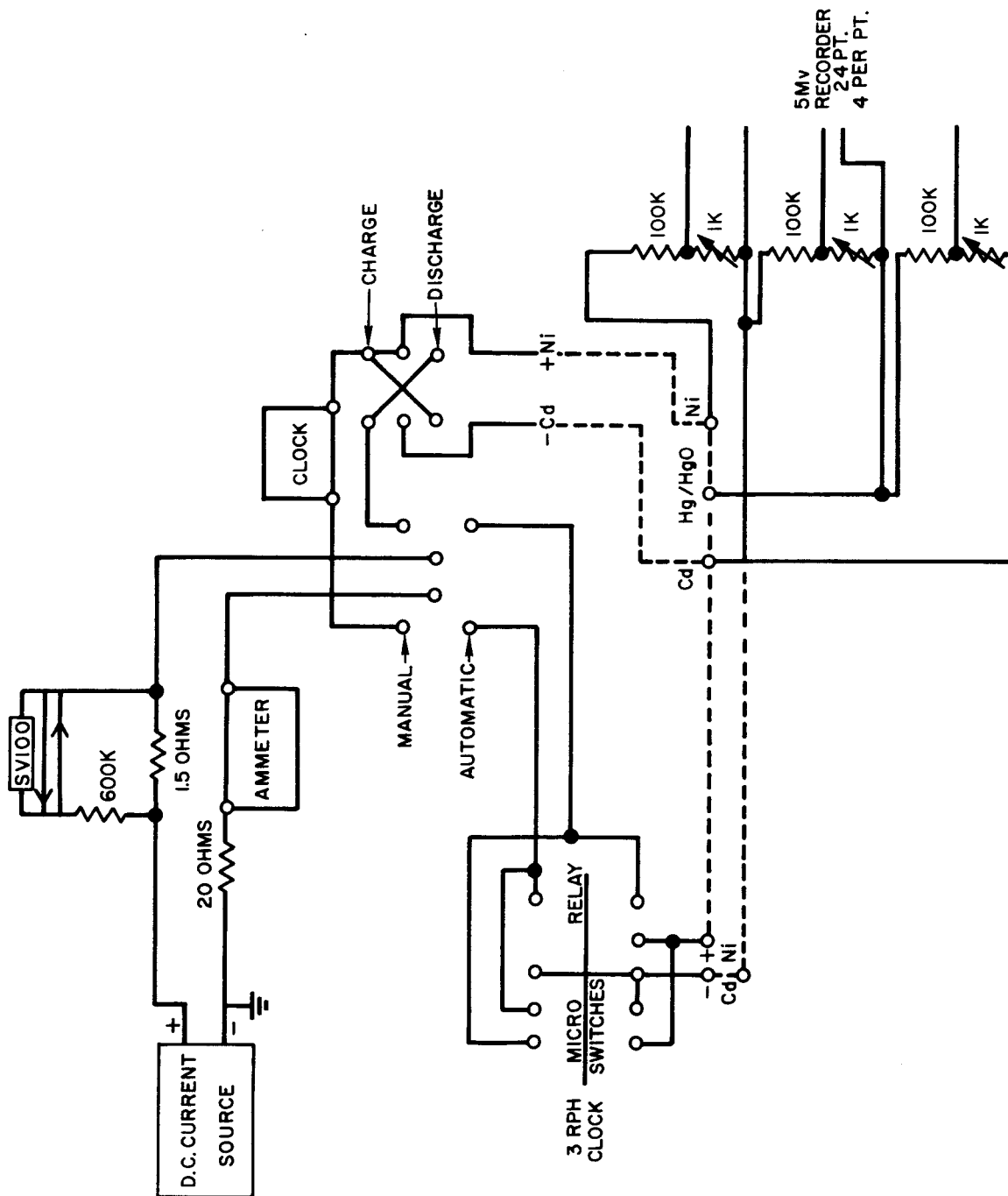
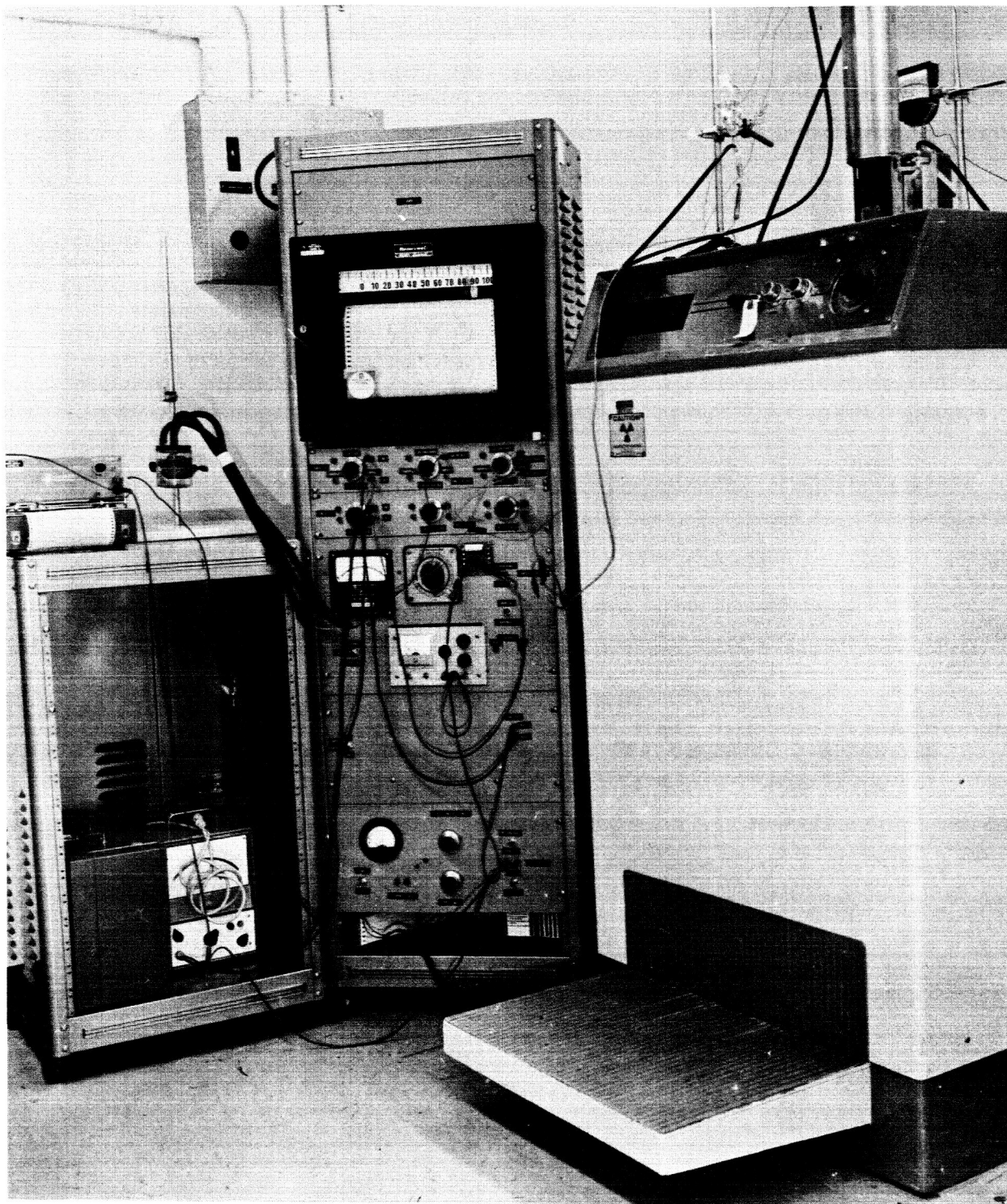


Figure 3. Circuitry for Ni-Cd Cell Cycling

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Figure 1. Test Cell Installed in Co-60 Source II

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are led out through stainless steel spiraled tubes coming up the column from the well. The salt bridge was also brought up through one of these tubes. After hookup, the well is closed with a stainless steel cover and then can be lowered automatically into the source. A lift, attached to a timer, is available to automatically raise the sample after a predetermined dosage.

## 2. Electron Source

The electron source was a Van de Graff accelerator capable of producing 2 Mev electrons at 5  $\mu$ a. The dosage was monitored by integrating the current resulting from the collection of the electrons on the electrodes.

## 3. Neutron Source

The neutron source was a small swimming pool reactor in which a port was available for sample irradiations with either thermal or fast neutrons. The fast neutron dose rate is  $6.6 \times 10^3$  rads ( $H_2O$ )/hr accompanied by gamma at  $8 \times 10^3$  rads ( $H_2O$ )/hr. The radiation dosage varied less than 10% from the center to the outer periphery of the cells.

# C. EXPERIMENTAL VARIABLES

## 1. Introduction

Experimental conditions had to be established in the laboratory with respect to the following variables: current density, type of cycle, length of cycle, state of charge about which to cycle, temperature and concentration of electrolyte.

## 2. Type of Cycle

The electrochemical effects on irradiated electrodes were investigated by following the voltage behavior of the cells during a cycling regime. Rather than the 90 min. cycle usually used in space applications, a 20 min. cycle was chosen, with 6 min. of charge, 4 min. open circuit, 6 min. discharge

and 4 min. open circuit. With this short cycle several cycles could be completed even during short irradiations.

### 3. Current

The effect of various currents on the cell voltage and other parameters of cell behavior was tested by operating cells at several currents. A high current, 0.40 amp, resulted in the electrodes becoming full of bulges and pockets due to either excessive local heating or excessive local gas evolution. In the length of cycle used, low currents of 0.10 amp or less gave little change in the voltages of the cells in going from open circuit to charge or discharge. An intermediate current of 0.20 amp was then chosen for use on all experiments. A Luggin capillary placed at various positions between the electrodes and behind the electrodes in a laboratory cell was used to determine that all the polarization was due to the resistance of the electrolyte. Several cells were cycled in the laboratory for extended periods of time at 0.20 amp current. In one such cell, cycled for 17 days at room temperature, a small amount of precipitate formed under the cadmium electrode. This precipitate was analyzed and found to contain cadmium and nickel in the ratio of 3.75:1. An identical experiment to confirm this observation was not performed and an explanation of this experimental result has not been attempted. It is known, however, that migration of active cadmium material does occur on the cadmium electrode.

### 4. State of Charge

With the current and cycle chosen one may calculate that a 5% change in state of charge occurs on either the charge or discharge portion of the cycle. Since normally the nickel-cadmium batteries on space missions are not discharged very deeply due to cycle life limitations, cycling about a state of charge of 70 to 75% was chosen for this investigation.



## 5. Electrolyte Concentration

Aqueous solutions of thirty and thirty-five percent KOH have been described in the literature<sup>3</sup> as suitable concentrations for nickel-cadmium batteries. In our preliminary experiments, negligible variations in IR drop, polarization and total capacity of the cells were observed over the range of 25% to 40% KOH. Therefore, 30% KOH solution was used for all experiments. A fresh solution was prepared for each experiment in order to keep carbonate contamination to a minimum.

## 6. Temperature

The logical temperature for the laboratory experiments was laboratory ambient temperature which varied between 22 and 25°C. It became apparent early in the study that temperature did cause large changes in voltage characteristics of the cells. Gamma Source II operates at a measured 45°C so laboratory runs were made at this temperature also. Although voltage reproducibility, upon temperature cycling a cell from 25° to 45°C and back to 25°C, was poor over 2-3 hour periods at each temperature, behavior was quite reproducible over 24 hour periods. Because of the effect of temperature on the voltage of these cells, a reference nickel-cadmium cell was usually run outside the source at the same temperature as the cell being irradiated. No sloughing off of material from the electrodes was ever observed in these external cells.

### III. IRRADIATION RESULTS

#### A. GAMMA IRRADIATIONS

##### 1. Introduction

The general procedure in this study was to irradiate for a long period initially, examine the system for damage and then reduce the dose to find at what level the damage first became apparent. Table I summarizes most of the experimental results from runs in the gamma sources and also those in the electron and neutron sources.

##### 2. Material Loss from the Electrodes

It was apparent from the very first run that some physical damage was occurring to the electrodes in that solid material was found on the bottom of the irradiated cell. This material was collected by filtration. The electrodes were washed using a wash bottle and the dislodged solids were combined with the precipitate. (An effort to insure complete removal of this loosened material by ultrasonic cleaning proved to be unsatisfactory. Ultrasonic treatment of cycled electrodes, whether irradiated or not, resulted in the loss of large amounts of material. No material loss had been obtained from similar treatment of uncharged non-cycled electrodes.) In a later experiment visual observation at half-hour intervals of a cell at open circuit conditions showed that clouding of the electrolyte began after one hour of irradiation in Source II, i.e.,  $1.4 \times 10^6$  rads ( $H_2O$ ). The lowest total dose for which an appreciable (i.e., weighable) amount of precipitate was obtained was  $5.8 \times 10^6$  rads ( $H_2O$ ).

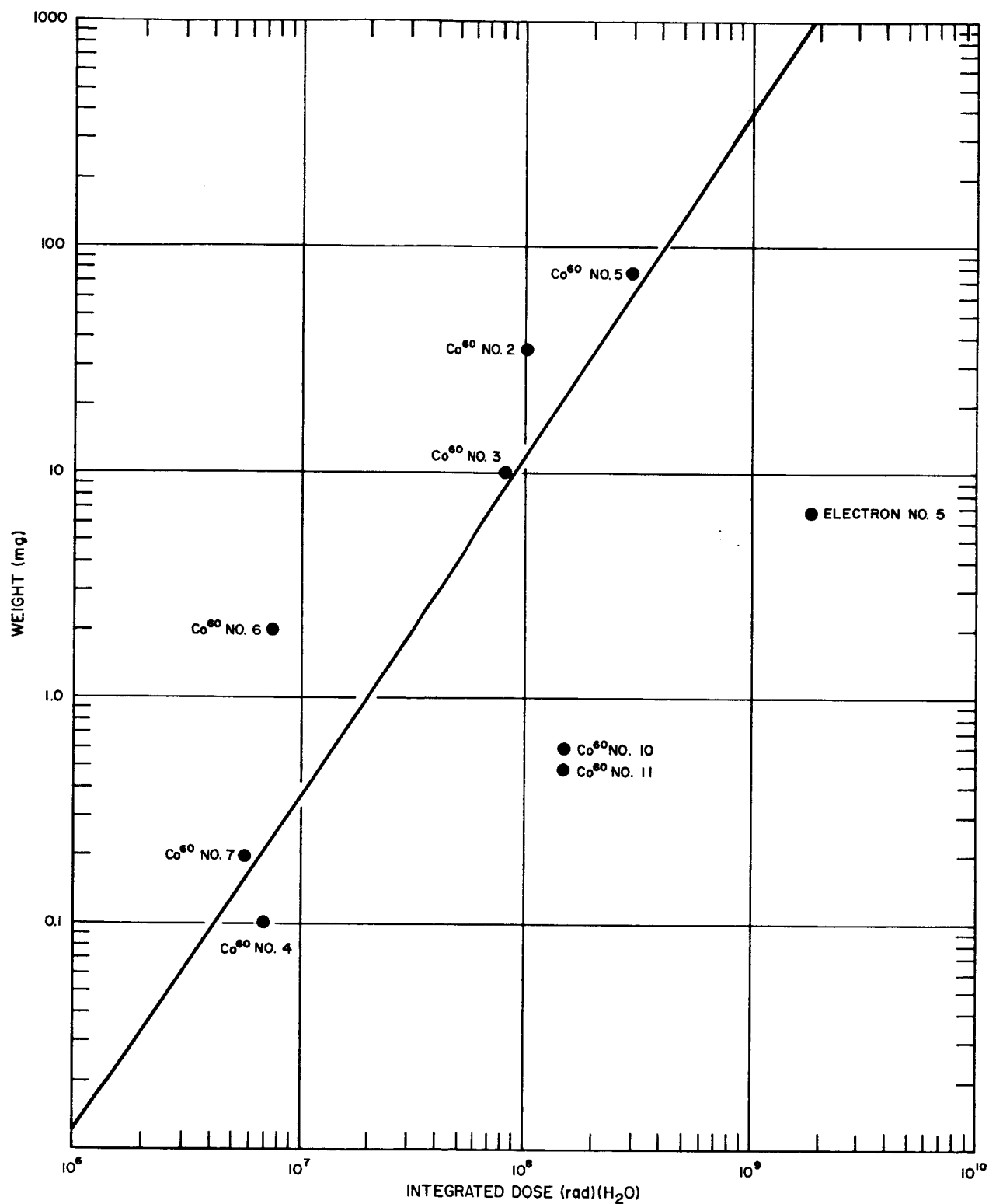
The amounts of material lost from the electrodes in relation to the total dose are plotted in Figure 5. The data show a monotonic functional

TABLE I. Summary of Results from Irradiations of Experimental Nickel-Cadmium Cells

Run #	Radiation Source	Dose Rate (rads/hr)	Length of Run (hr)	Total Dose (rads)	Weight of Material Sloughed (mg)	Cd to Ni Ratio in Sloughed Material	Sloughed Rate (mg/hr)	Temp. (°C)	Type Cell	Remarks
Co-60 #1	Source II	$1.4 \times 10^6$	12	$1.7 \times 10^7$	Contami-nated	10:1		45	Quartz	On cycling
Co-60 #2	"	$1.4 \times 10^6$	72	$1.0 \times 10^8$	35.6	6:1	.50	45	"	" "
Co-60 #3	"	$1.4 \times 10^6$	62	$8.7 \times 10^7$	10.1	7:1	.15	45	"	" "
Co-60 #4	"	$1.4 \times 10^6$	5	$7 \times 10^6$	.1	NM	.02	45	"	Open circuit
Co-60 #5	"	$1.4 \times 10^6$	215	$3 \times 10^8$	77	3:1	.36	45	"	On cycling
Co-60 #6	Source I	$8 \times 10^4$	96	$7.7 \times 10^6$	2	NM	.02	30	Lucite	" "
Co-60 #7	"	$8 \times 10^4$	72	$5.8 \times 10^6$	.2	NM	.003	30	"	" "
Co-60 #8	"	$8 \times 10^4$	168	$1.3 \times 10^7$	.2	NM	.001	30	"	" "
Co-60 #9	Source II	$1.4 \times 10^6$	111	$1.5 \times 10^8$	NW			45	Commercial	Open circuit
Co-60 #10	"	$1.4 \times 10^6$	111	$1.5 \times 10^8$	5.9	40:1	.05	45	Stainless steel	On cycling
Co-60 #11	"	$1.4 \times 10^6$	110	$1.5 \times 10^8$	4.1	3:1	.04		"	" "
Electron #1	Van de Graff	$4 \times 10^9$	.5	$2 \times 10^9$	NW				Polystyrene	(this summarizes four runs)
Electron #5	"	$4 \times 10^9$	.5	$2 \times 10^9$	6.5	10:1	13.00	50	Quartz	Open circuit
Neutron #1	Reactor	$1.5 \times 10^4$	52	$7.4 \times 10^5$					"	On cycling

NM = not measured - amounts too small

NW = not weighed - usually less than .1 mg



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Figure 5. Weight of Sloughed Material vs Integrated Dose

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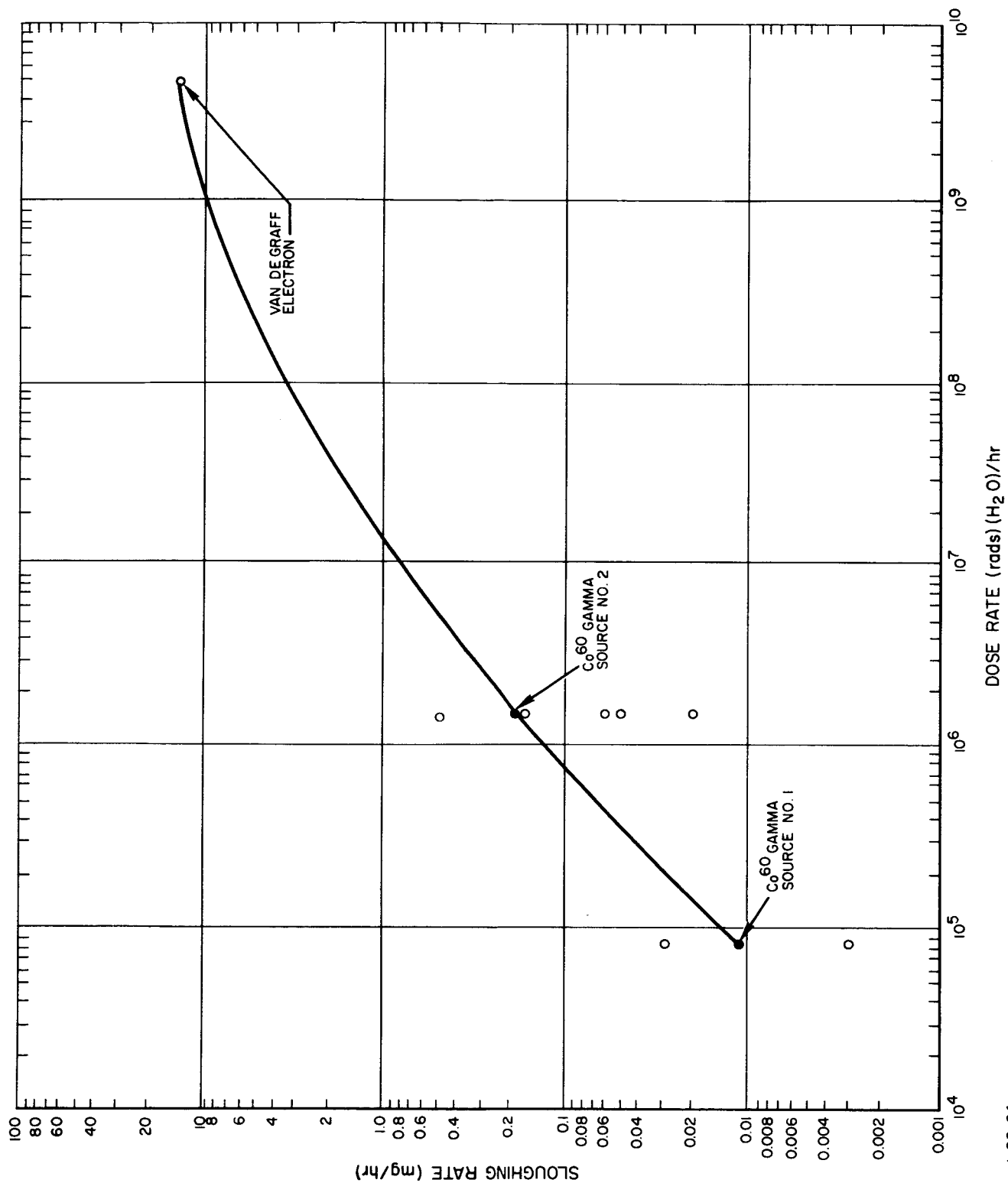
relationship but are not closely correlated by this technique. Runs #10 and 11 seem abnormally low in the amount of material lost or sloughed. These runs were made in the sealed stainless steel cell where evolved gases were retained in the cell. Other than this difference in experimental technique, no explanation for the low results of runs #10 and 11 is available.

The relationship of the rate at which the material was sloughed and the dose rate is also of interest. Table II summarizes these data. The data are averaged and are plotted in Figure 6. The results suggest that the rate of material loss is approaching an asymptote with respect to the dose rate if the electron irradiation results are included in the correlation. With heavier particle radiations, in this case electrons as compared to gammas, larger groups of radicals are formed in the track and can recombine there; thus fewer are able to diffuse away to react as free radicals. This effect is called the linear energy transfer effect (LET). Its significance in this work may be small, but the apparent trend should be considered as tentative in view of possible effects associated with the different types of radiation.

When a sufficient quantity of residue (2 mg) was available from gamma and electron irradiation, it was analyzed with an emission spectrograph. In some runs in which there was no measurable amount of residue, all the electrolyte was neutralized and evaporated to dryness. Representative samples of these evaporated residues were then analyzed. The results of all these analyses are shown in Table III. Some sacrifice in precision of the nickel and cadmium analyses was made in order to include all the trace elements in the determination. Where sufficient material was available the samples were analyzed again specifically for the cadmium to nickel ratio, as this quantity seemed to be significant. These results are given in Table IV. The trace

TABLE II. Relation of Rate of Loss of Electrode Material and Dose Rate

Run #	Rate of Material Loss (mg/hr)		Dose Rate (rads/hr)
Co-60 #6	0.027	} Av. 0.011	$8 \times 10^4$
Co-60 #7	0.003		$8 \times 10^4$
Co-60 #8	0.003		$8 \times 10^4$
Co-60 #2	0.5	} Av. 0.19	$1.4 \times 10^6$
Co-60 #3	0.15		$1.4 \times 10^6$
Co-60 #4	0.02		$1.4 \times 10^6$
Co-60 #5	0.36		$1.4 \times 10^6$
Co-60 #10	0.06		$1.4 \times 10^6$
Co-60 #11	0.05		$1.4 \times 10^6$
Electron #5	13		$4 \times 10^9$



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Figure 6. Rate of Material Loss from Electrode vs Dose Rate

TABLE III. Emission Spectrographic Analyses of Cell Residues

Column	1	2	3	4	5	6	7	8	9	10	11	12
Sample #	1st Co-60 Run	2nd Co-60 Run	3rd Co-60 Run	5th Co-60 Run	10th Co-60 Run	Neutron Residue Irrad.	Van de Graff	Residue fm. Rm. Temp. Cycling	Nonirradiated Cd Electrode Material	Nonirradiated Ni Electrode Material	Irradiated Comm'l Cell Residue	Nonirradiated Comm'l Cell Residue
Total Dosage in Rads (H <sub>2</sub> O)	1.7x10 <sup>7</sup>	1.0x10 <sup>8</sup>	8.7x10 <sup>7</sup>	3.8x10 <sup>8</sup>	1.5x10 <sup>8</sup>	7.4x10 <sup>5</sup>	2x10 <sup>9</sup>					
Ag	.02	.02	.3	.03	.01	.001	N.D.	.3	.3	.1	N.D.	N.D.
Al	.3	.4	.3	.2		.2		.3	.5		.003	.002
B	.03	.1	.05	.01	.05	.005		.1			.002	.003
Ba	.3	.01						.3		.03		
Ca	1.	.1	.1	.1	.1	.1		2	.3	.3	.075	
Cd	3	.1	10	M***	.1	.002	.01	10	10	.5	.1	.02
Cr	.01	.05	.05	.01		.01		1	.01	.1	.001	
Cu	.3	.03	5	1	.1	.01		.3	.05	.05	.02	.01
Fe	.1	.2	.2	.3	.03	.01		.2	.05	.1	.05	.008
Li	.01	.01										
Mg	.02	.005	.05	.2	.1	.002		.01	.05	.05	.005	.002
Na	3	.5	.2		.001	.002	.003	.3	.8	.4	.1	.1
Ni	.05	.05	1	1	.1	N.D.	.001	3	10	10	.1	.03
Pb	.1	.01	.5	.3	.1			.05		.05	.004	.005
Si**	4	10	2	1	.1	.05	.02	.3	.2	.2	.03	.02
Sn	.05	.01	.05		.001							
W*	2	.5										
Zr	.05	.5	.05									
Co			.1	.5	.05					.2	.03	

\*\*\* Major constituent - the later ratio determination does not give specific values for Ni or Cd

\*\* Silicon high in almost all samples because evaporation and filtration carried out in Pyrex glassware

\* Tungsten lead used and it etched through

Column 6 is the analysis of a representative evaporated residue from the neutron irradiations. Column 8 is the analysis of the material found under the cadmium electrode after the 17 day room temperature cycling was complete. Columns 9 and 10 are analyses of electrode materials exclusive of the steel skeleton of the electrode. Columns 11 and 12 are materials washed from the separator in the commercial cells; both were charged, discharged to 75% and cycled identically. The material described in 11 was from a cell which was irradiated and the material in 12 was from a non-irradiated cell. The separator from the irradiated cell was black from this material whereas the non-irradiated separator was not discolored.



TABLE IV. Cadmium/Nickel Ratio of Sloughed Material

Experiment	Cd/Ni Ratio	Wt. of Mat'l (mg)	Total Dose (rads)
Co-60 Run #10	40:1*	5.9	$1.5 \times 10^8$
Co-60 Run #11	3:1*	4.1	$1.5 \times 10^8$
Co-60 Run #1	10:1	low+	$1.7 \times 10^7$
Electron Run #5	10:1	6.5	$2 \times 10^9$
Co-60 Run #3	7:1	10.1	$8.7 \times 10^7$
Co-60 Run #2	6:1	35.6	$1.0 \times 10^8$
Co-60 Run #5	3:1	77	$3 \times 10^8$

\* Only rough analyses were possible on these samples - therefore, the ratios are not as reliable as those of the other runs.

+ Contaminated by tungsten but amount was less than 5 mg.

TABLE V. Spectrographic Analyses of Residues from Individual Electrodes

Electrode & State of Charge	Wt. % Cd	Wt. % Ni*
Cd 0%	.02	ND
Cd 75%	.005	ND
Cd 100%	.005	ND
Ni 0%	.005	ND
Ni 75%	.01	ND
Ni 100%	.01	ND

\* Remainder of residue was KCl. Nickel concentration was below detection limit of 0.05%.

elements found in the residues correspond to those expected from the materials used in cell manufacture. The high percentage of cobalt found may be ascribed to the high cobalt content usually found in nickel. X-ray analysis of the material from Run #5 showed  $\text{Cd}(\text{OH})_2$  and  $\text{SiO}_2$  to be the predominant identified components. There were a large number of unidentified lines in the x-ray pattern but none appeared to be attributable to nickel or nickel compounds. Contrary to this result, particles of sloughed material were found to line up in a magnetic field, indicating the presence of some ferromagnetic component such as nickel metal.

A significant correlation is also found if the cadmium to nickel ratios in the sloughed material are compared to the weight of material lost. Table IV shows these results. It should be noted that the greater the amount of material lost, the lower the ratio of cadmium to nickel. The electron irradiation results again are included and follow the trend.

Individual electrodes in 30% KOH were irradiated in separate unconnected plastic cells. The data obtained are summarized in Table IV. The electrodes were at various states of charge as indicated. Sufficient amounts of precipitate were not available for the usual filtering and analysis technique. The electrolyte together with the small amount of precipitate was neutralized with hydrochloric acid and evaporated to dryness. The analyses were then made on the residue.

These data do not show conclusively which electrode is contributing the most to the sloughing. There is a trend in the weight percent of cadmium with state of charge which would indicate that the hydrated cadmium hydroxide is more susceptible to the sloughing mechanism than is the cadmium metal. In the discharged state the cadmium is present as the hydroxide on the cadmium electrode and in the charged state as the metal. Thus the amount of cadmium

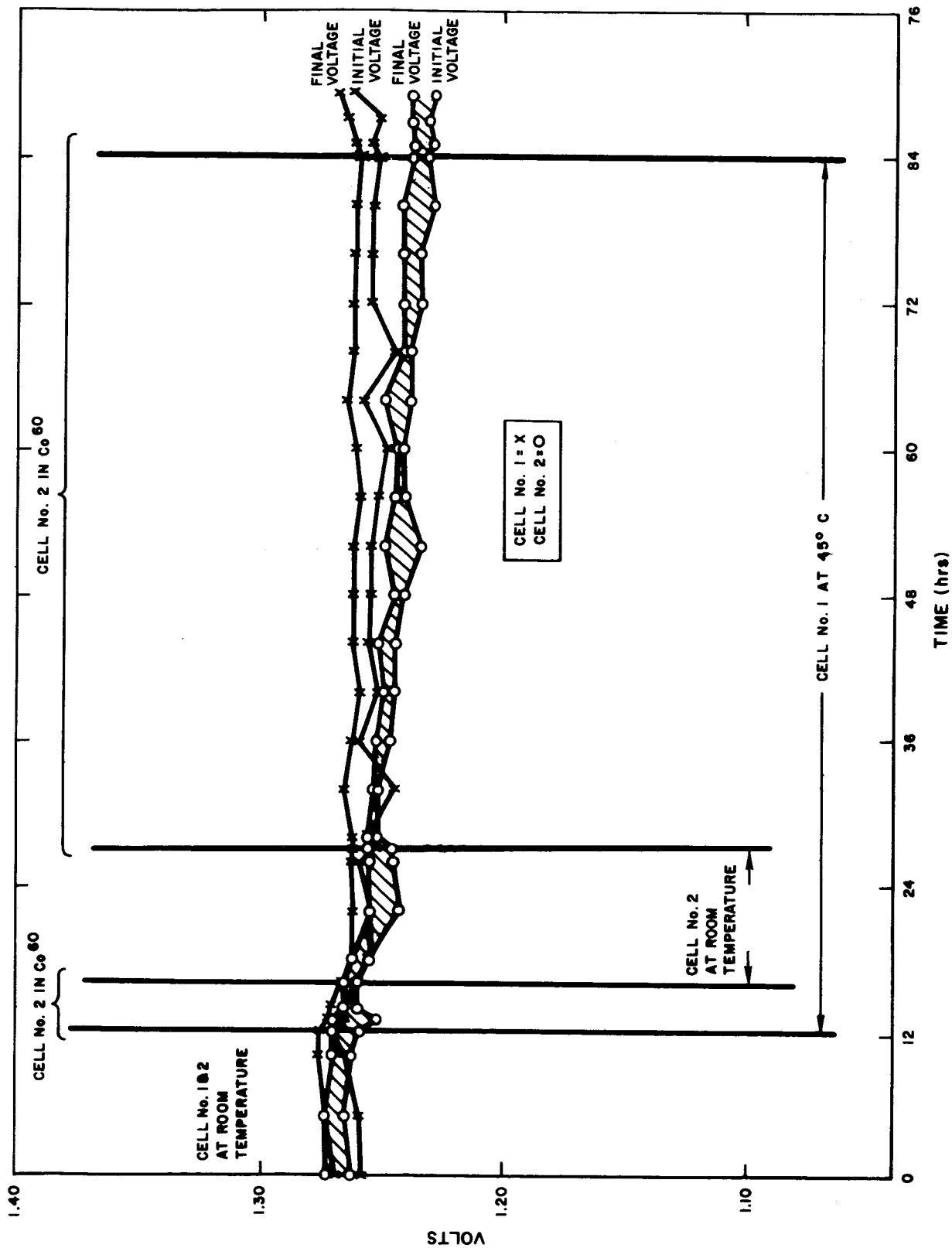
lost from the cadmium electrode is low for the 75% and 100% charge cases but high for the discharged condition. Loss of material from the electrodes also occurred when commercial cells were irradiated; these results are presented below in Section 5.

### 3. Electrochemical Effects

A change in cell voltage was expected as one of the effects of radiation. This change was anticipated to arise from polarization caused by gas evolution during radiolysis of the electrolyte. These gases might tend to adhere to the surface of the electrode causing a higher IR drop. In addition, a change in electrode capacity might be expected from the sloughing off of material from the electrodes. A loss of capacity, in addition to that which would be caused by actual loss of material, could also be caused by (1) the uptake of oxygen by the cadmium electrode, and (2) the actual radiolysis of the active material, such as the  $\text{NiOOH}$ , in the electrode.

Two different electrochemical phenomena were observed in two separate runs. In Run #3 the voltages of the cell being irradiated and the  $45^\circ\text{C}$  reference cell diverged progressively to a difference of 10 mv at the end of 62 hours as is shown by the open circuit voltage in Figure 7. Unfortunately, in the longer run of 215 hours, #5, a similar measurement could not be made due to failure of the reference cell. This phenomenon of a cell failing for no apparent reason had been observed before in the laboratory. In all other long runs no reference cell at  $45^\circ\text{C}$  was used so that no long term voltage effect was measured.

After the 215-hour run in Gamma Source II (Run #5), the cell was discharged at the 0.2 amp rate. It was noted that the cadmium electrode became the electrode limiting the total capacity of the cell, as shown in



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Figure 7. Open Circuit Cell Voltage During Third Co-60 Gamma Irradiation

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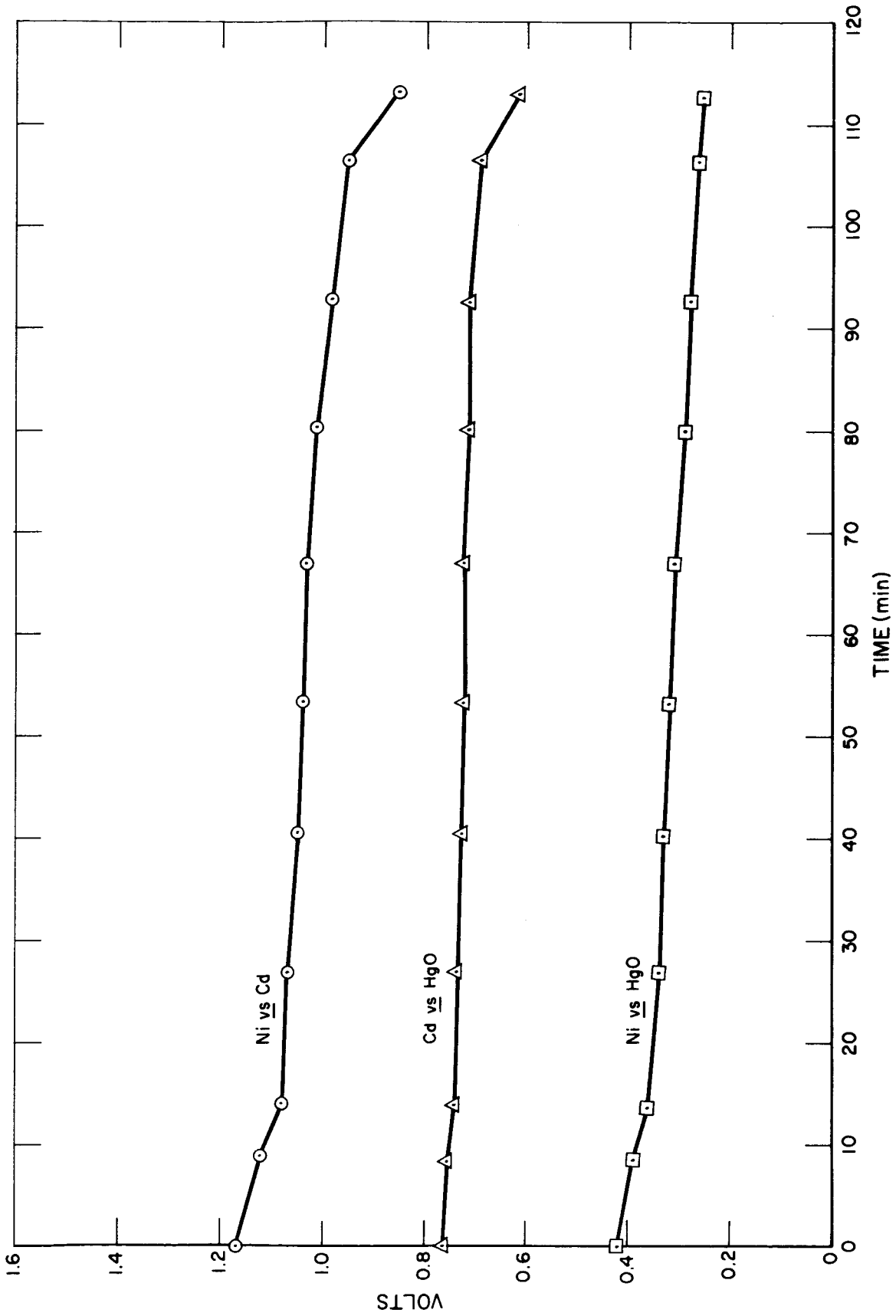
the discharge curve of Figure 8, recorded after a complete discharge and charge cycle of this cell. Tests on such cells before irradiation invariably have shown that the nickel electrode limits the cell capacity at about 0.4 ampere-hour (120 minute discharge at 0.2 amp). This change was observed only in the one long run.

During the initial discharge of the cell after the 215 hour irradiation, the cell and specifically the cadmium electrode, went through a 70 mv voltage step downward after approximately 1/3 discharged. Upon recharging the cell, this step did not appear nor did it reappear on subsequent discharge. No explanation is apparent for this single observation.

#### 4. Gas Evolution

A stainless steel cell with a quartz liner (Figure 2) was constructed to measure gas evolution. Two runs were made in this cell. The pressure transducer in these measurements was a diaphragm type which has a voltage output of 5 mv per psi. The sensitivity of the transducer was 0.1 psi over 0-20 psig. Run #10 was the first run with the stainless steel quartz-lined cell. Figure 9 shows the variation of the measured cell pressure with time during this run. The important features of this curve are: (1) the initial drop in pressure, due to oxygen uptake by the cadmium electrode, (2) a rapid increase in pressure upon placing the cell in the source, due to two factors, (a) the temperature rise and (b) the radiolysis of the solution giving oxygen and hydrogen gas, (3) a further steady pressure increase due to radiolytic gas production and (4) a pressure decrease on removal of the cell from the source due to temperature decrease and oxygen uptake by the cadmium electrode.

During the run the cadmium electrode continues to take up some of the oxygen so that the resultant pressure is due to a variety of factors. The



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Figure 8. Discharge Characteristics of Nickel-Cadmium Cell After Co-60 Gamma Irradiation No. 5

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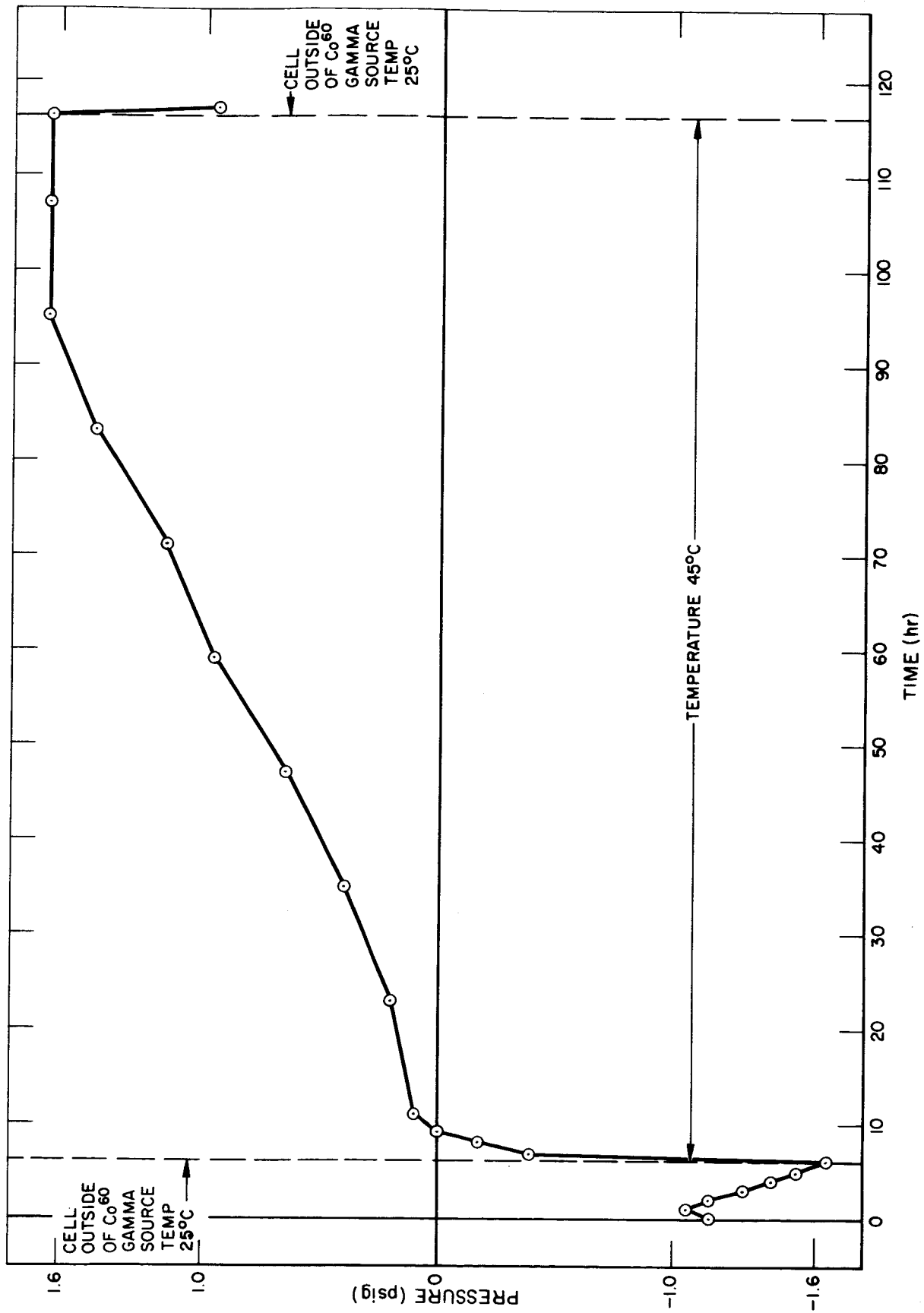


Figure 9. Pressure Changes During Gamma Irradiation No. 10

constant pressure region towards the end of the irradiation is, at present, difficult to explain. A steady state between radiolysis, producing oxygen, and cadmium electrode reaction with oxygen is a possible explanation but this is only conjecture.

An electrical short in the pressure transducer cable occurred in Run #11 due to insulation breakdown in the cable because of radiation. Only the pressure data from the initial part of the run and the final pressure were obtained. The final decay of pressure due to temperature drop and the cadmium electrode-oxygen reaction, after the cell was removed from the source, was also measured. Where comparisons were possible these data confirmed those of Run #10.

Table VI summarizes the results of the gas analyses. A valve leak and air contamination occurred at the conclusion of Run #10. This occurrence probably decreased the hydrogen result and may have lowered the CO and CH<sub>4</sub> concentration below the detection limit. In Run #11 the methane and carbon monoxide probably arise from the action of radiolytically produced hydrogen atoms on some carbon-containing compound. The origin of the carbon-containing compound has not been determined but may arise from carbonate in the electrolyte, from the electrode binder or from the neoprene "O" ring seal in the stainless steel cell.

TABLE VI. Pressure Increase and Gas Analyses of Gamma Runs #10 and #11

	Pressure Increase (corrected for temp.)	Gas Analysis (Vol. %)				
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO
Run #10	2.6 lbs	2.1	18.4	79.6	0	0
Run #11	2.3 lbs	8.1	1.2	90.2	.17	.05



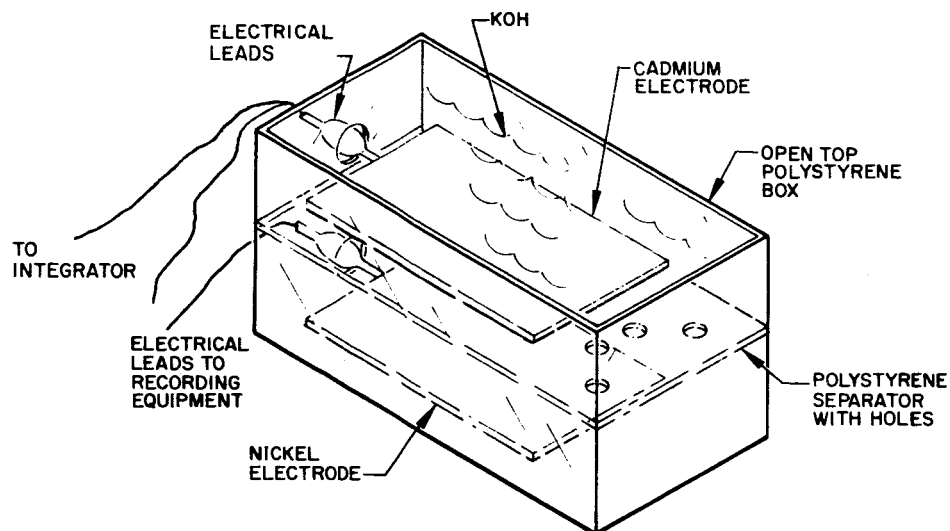
## 5. Commercial Cell Irradiations

Several commercial cells (5 electrodes in a plastic case) on open circuit were irradiated in Gamma Source II. These cells were fully charged, discharged to 75% of capacity, and then cycled for 24 hours, as described earlier for the laboratory cells, prior to the irradiation. These cells after irradiation were bulging considerably due to gas buildup in the cell. Upon opening the cells, sloughed material was observed on the separator but only where it was in contact with the nickel electrode. The cadmium to nickel ratio of this material was 2:1. The amount obtained was not weighed. The loss of this material from the Ni electrode appeared to have no measurable effect ( $\pm 2\%$ ) on the capacity of the cell which was determined before and after the irradiation.

### B. ELECTRON IRRADIATIONS

Two types of cells were used for these irradiations. Figure 10 shows the cells used for the first four irradiations in which the electrodes were perpendicular to the 2 Mev electron beam. The last experiment (Run #5) was done with the electrodes in the lower portion of the quartz cell described previously (see Figure 1). Thus, the electrodes in this case were parallel to the beam. Instrumentation of the electron source required that the cells be left on open circuit during these irradiations. A decrease of about 30 mv in this voltage occurred but was thought to be entirely due to the increase in temperature, which reached 52°C. A reference cell was not used for comparison during these short runs because of the uncertainty in temperature across the cell.

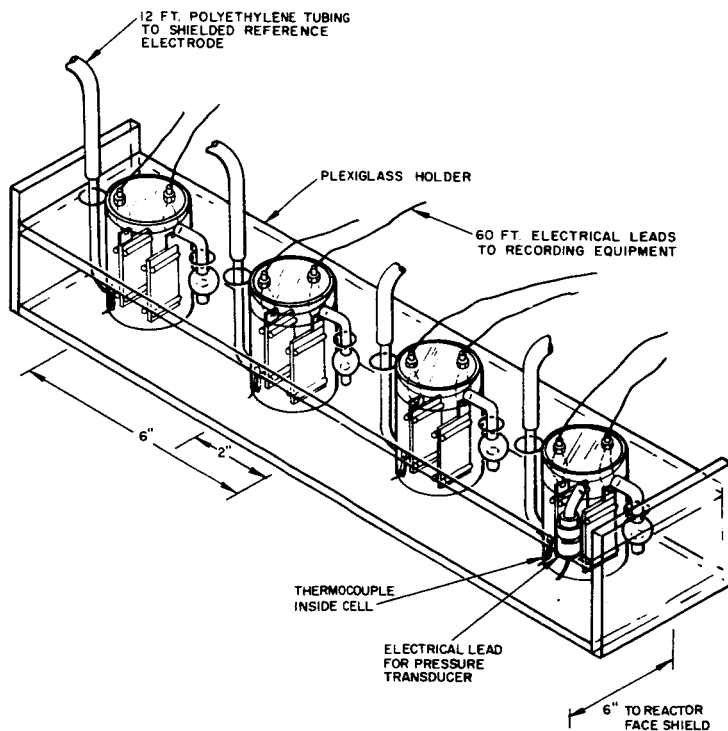
Table VII summarizes the results of these runs. In Runs #1 through 4 only one electrode was irradiated per run and, due to absorption by the



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Figure 10. Nickel-Cadmium Cell Used in 2 Mev Electron Accelerator Experiment



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Figure 11. Quartz Cell Used in Fast Neutron Irradiation Experiments

electrode, the penetration of the electron beam was small. In the fifth run, the electron beam impinged primarily on the electrolyte. Thus, in the first four runs, the upper electrode was covered with only a little electrolyte, and the amount of radiolysis occurring was small. In the last run, the electrolyte received more radiation and sloughing was observed. Thus these results are consistent with radiolysis of the electrolyte playing a role in the loss of material from the electrodes. The weight and analysis of the material sloughed in Run #5 correlates reasonably well with that obtained in the Co-60 irradiations as is shown in Figures 5 and 6. In contrast to the gamma irradiations, a steep gradient in energy absorption probably occurs in the electron irradiations.

TABLE VII. Electron Irradiation Results

Run #	Electrode Exposed	Sloughed Material (mg)	Dosage (rads H <sub>2</sub> O)
1	Ni	None	$5 \times 10^8$
2	Cd	"	$5 \times 10^8$
3	Ni	"	$2 \times 10^9$
4	Cd	"	$2 \times 10^9$
5	Both	6.5	$2 \times 10^9$

### C. NEUTRON IRRADIATION

Figure 11 shows the physical arrangement of the cells for our neutron irradiation. The cells were irradiated for 52 hours for a total dosage ( $\gamma$  and n) of  $7.4 \times 10^5$  rads. No sloughing of material from any of the electrodes was observed. Some transmutation reactions had occurred. The

post-run gamma spectra, indicating the predominant peaks, are shown in Figures 12 and 13. The nuclides formed and their mode of production are summarized in Table VIII. The formation of  $\text{Cd}^{115}$  (Figure 12) is further proof that cadmium is present in the nickel electrode. The post-run examination of the electrolyte showed only the beta radiation due to potassium 41. Evaporation of the electrolyte and subsequent spectrographic analysis showed a trace of cadmium present but no evidence of any nickel.

TABLE VIII. Nuclides and Their Mode of Production

Electrode	Nuclide	Half Life	Mode of Production
Cadmium	$\text{Cd}^{115}$	53 hr.	$\text{Cd}^{114}(\eta, \gamma)\text{Cd}^{115}$
	$\text{Cd}^{107}$	6.7 hr.	$\text{Cd}^{106}(\eta, \gamma)\text{Cd}^{107}$
	$\text{Co}^{58}$	71 days	$\text{Ni}^{58}(\eta, \gamma)\text{Co}^{58}$
Nickel	$\text{Ni}^{65}$	2.56 hr.	$\text{Ni}^{64}(\eta, \gamma)\text{Ni}^{65}$
	$\text{Co}^{58}$	71 days	$\text{Ni}^{58}(\eta, p)\text{Co}^{58}$
	$\text{Co}^{60}$	5.26 yr.	$\text{Co}^{59}(\eta, \gamma)\text{Co}^{60}$
	$\text{Cd}^{115}$	53 hr.	$\text{Cd}^{114}(\eta, \gamma)\text{Cd}^{115}$

The fact that no sloughing was observed is consistent with the results obtained from Co-60 irradiations in which a dose of  $1.4 \times 10^6$  rads ( $\text{H}_2\text{O}$ ) was required to observe any effects associated with sloughing. This source did not provide neutrons only; however, from the very limited information available, it would appear that fast neutrons are not a great deal more damaging than gamma radiation with respect to material loss from the electrodes.

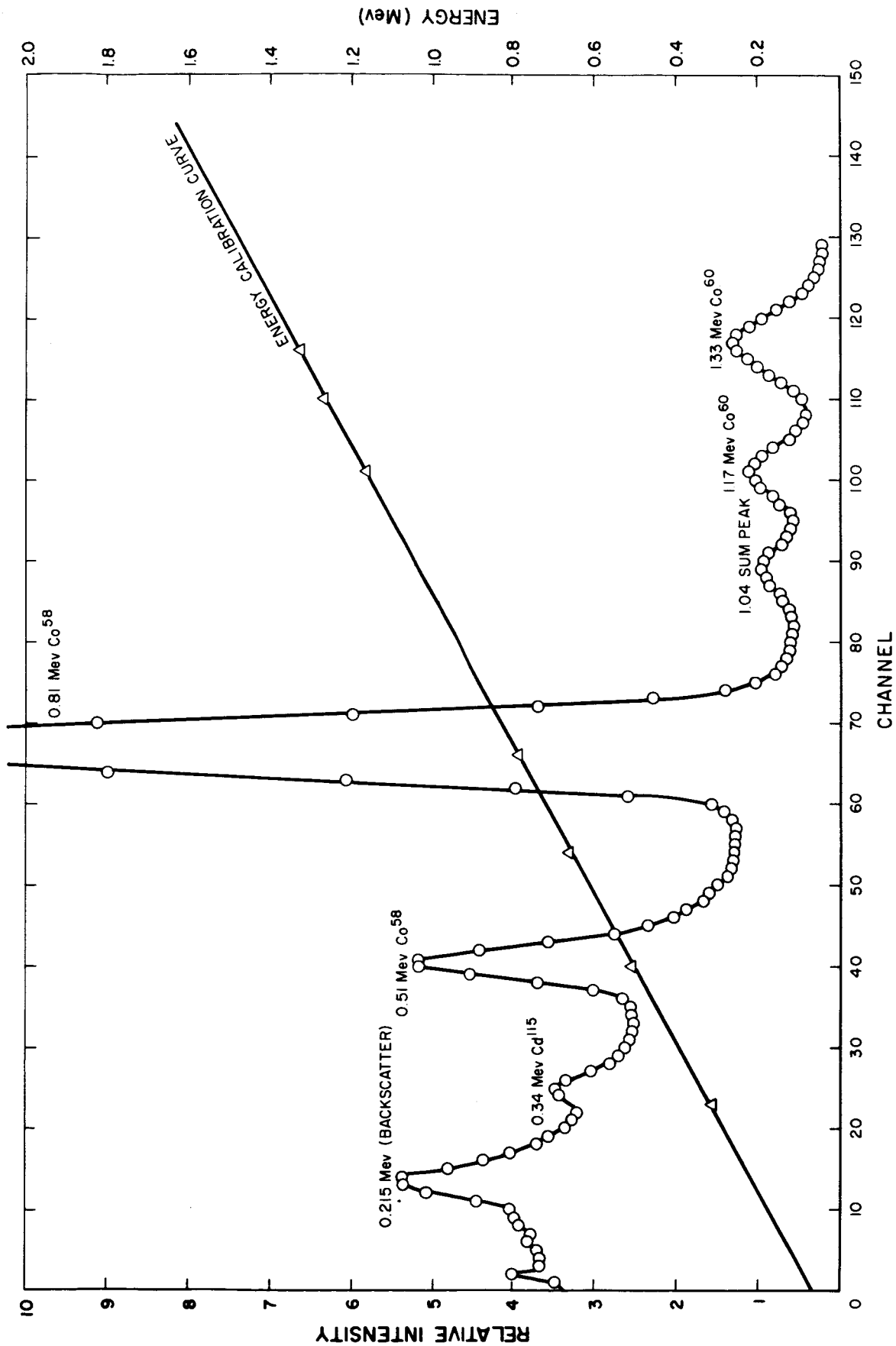


Figure 12. Gamma Counting of Nickel Electrode After Neutron Irradiation

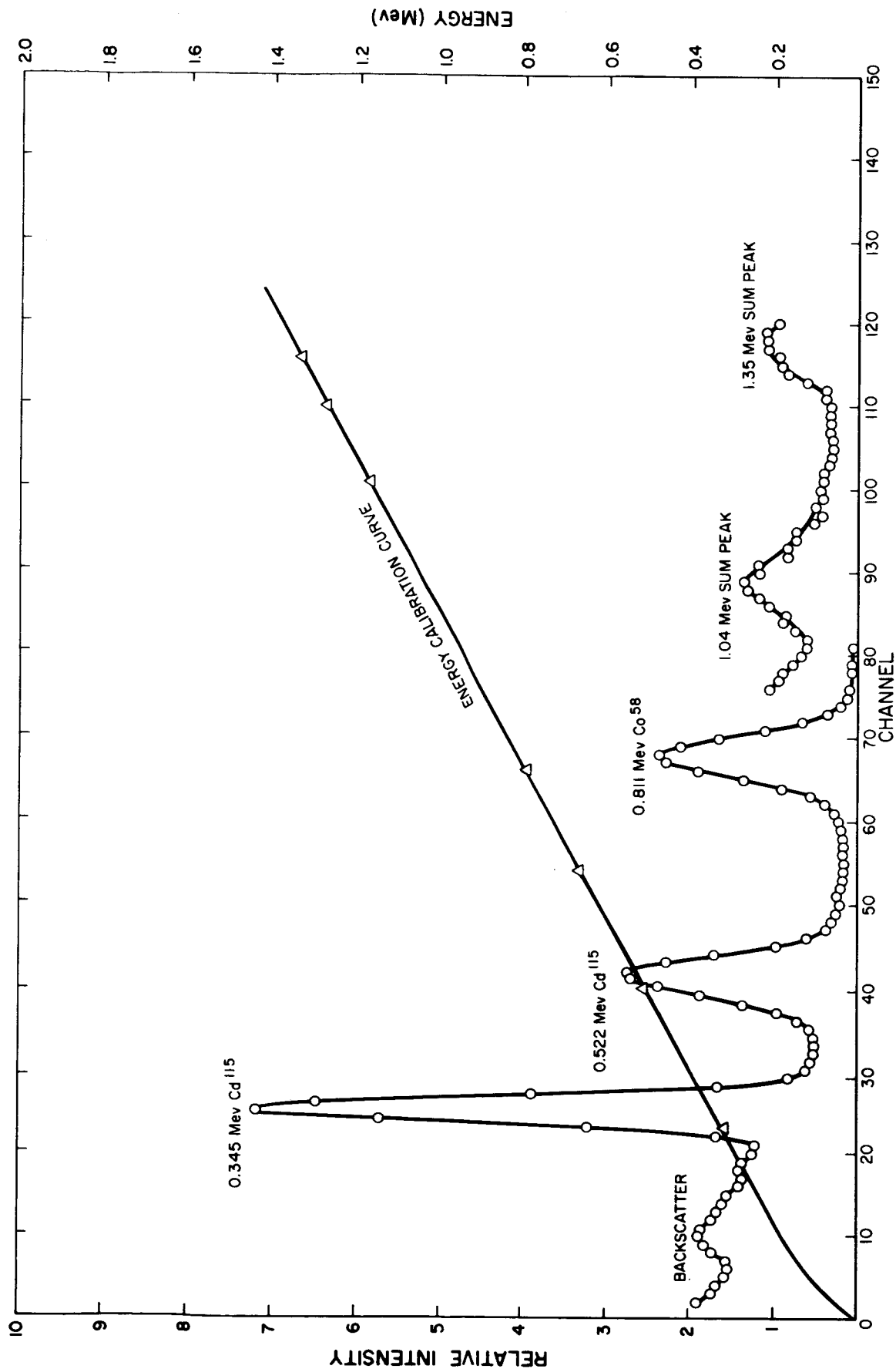


Figure 13. Gamma Counting of Cadmium Electrode After Neutron Irradiation

#### IV. DISCUSSION OF GAMMA IRRADIATION RESULTS

##### A. MATERIAL LOSS FROM ELECTRODES

###### 1. Mechanisms of Material Loss

Three mechanisms appear as possible causes for the sloughing phenomenon observed to accompany irradiation of the nickel-cadmium cells. Any or all of these may be causing this phenomenon. These mechanisms are:

###### a. The Mechanical Effect of Rapid Gas Evolution Resulting from Hydrogen Peroxide Decomposition

Hydrogen peroxide is formed in the electrolyte by radiolytic action. This peroxide is decomposed to form oxygen gas and water either by radiolysis or by the catalytic effect of the highly active electrodes. The oxygen evolved either inside or outside the electrodes may mechanically dislodge material from them. To test the possibility of this sequence of events, the effect of 1% hydrogen peroxide in 30% KOH on nickel and cadmium electrodes was observed in the laboratory. Oxygen gas was evolved at both electrodes but material was found to be dislodged from the nickel electrode only. Analyses showed this material to contain both nickel and cadmium. It is therefore possible to say that decomposition of hydrogen peroxide at the nickel electrode may lead to material loss from that electrode. The effect of lower concentrations of hydrogen peroxide should also be investigated; the steady state concentration of hydrogen peroxide in these irradiations is probably between 0.1 and 0.5 millimoles/liter<sup>4</sup> or three orders of magnitude less than the 1% concentration.

###### b. The Chemical Action of Hydrogen Peroxide

Hydrogen peroxide may react with specific materials on the electrodes. Peroxide may act as either a strong oxidizing or reducing

agent in basic solution. The oxidizing action is the more likely for the conditions of this study, with one possible action being on the porous nickel structure of the electrodes. This action, for example, may weaken the structure and lead to the loss of material from the electrodes. The experimental result with 1% hydrogen peroxide, mentioned in the previous section, may also be evidence for chemical attack by the peroxide. Some particles in sloughed material were observed to be attracted by a magnet. This mechanism and the one below could lead to nickel metal being present in the sloughed material. The nickel, of course, is ferromagnetic and would be attracted by a magnet.

c. The Chemical Action of Free Radicals

Hydroxyl free radicals may react with the materials of the electrodes. The reaction would release large amounts of energy and could in themselves be responsible for dislodging the material from the electrodes. While some cause of the sloughing phenomenon other than those associated with the radiolysis of the electrolyte is possible, it does not appear as likely.

It does not appear possible at present that any of the three mechanisms indicated above can be discarded as possible causes of this material loss.

2. The Origin of the Sloughed Material

There is a trend that the higher the total dose the greater the amount of material lost from the electrodes. From the Cd:Ni ratios of the sloughed material, it is evident that more cadmium is dislodged than nickel. Wet analysis of the electrodes, exclusive of the steel skeletons, showed that 2.5% of the nickel electrode was cadmium and about 25% of the cadmium electrode was cadmium, with nickel making up the remaining percentages of metals. Information



from the battery supplier indicates that cadmium tends to migrate and is expected to be on the surface of both electrodes. In this case, material dislodged first would naturally be richer in cadmium than in nickel for either electrode. However, as more material is removed, the Cd/Ni would be expected to change rapidly only for material coming from the nickel electrode.

The results of the Cd/Ni ratios in the sloughed material, therefore, are consistent with the view that the nickel electrode is contributing most to the sloughing. Additional evidence that the nickel electrode is the principal source of sloughed material is: (a) Individual electrode irradiations (Table V) show more cadmium coming from the nickel electrode than the cadmium electrode for the state of charge conditions of the experiments. (b) When complete commercial cells are irradiated, dislodged material is only found on the separator next to the nickel electrode. Further studies of this material loss from electrodes using compartmented cells will be needed to resolve this problem.

### 3. The Effect of Material Loss and Oxygen Evolution on Electrode Capacity

The largest amount of material lost from the electrodes in any one run was 77 milligrams. From the spectrographic analyses of this material the amounts of cadmium and nickel species were estimated to be approximately 40 mg. and 15 mg. respectively. If all of this material came from the nickel electrode it would have no discernible effect on the electrode capacity as 15 mg. corresponds to a maximum of 1.1% of the amount of active nickel material. (The latter was calculated from the 0.4 amp-hr observed capacity of this electrode.)

The cadmium electrode, from chemical analyses, contains about 1.0 gm of the metal which, if all active, corresponds to a 20% excess over the

0.4 amp-hr capacity. If the material all came from the cadmium electrode, the change in capacity again would not be discernible as 40 mg. amounts to only about 4% of the active cadmium material present. Thus, one may conclude that the sloughing off of material from the electrodes is not a principal contributor to the observed decrease in capacity of the cadmium electrode.

Oxygen from the radiolytic decomposition of the electrolyte will react at the cadmium electrode. In Run #10, approximately 60 cc of oxygen were produced which, if all reacted with the cadmium electrode, would oxidize and thus discharge 0.3 g of cadmium metal on the electrode. Considering the fact that there is only about 1 gram of cadmium (of which about 0.8 g is needed for full capacity) on the cadmium electrode, this indeed would change its capacity. Although a discharge curve was not recorded for Run #10 it was recorded for the apparently identical Run #11 and the discharging of the cell after the irradiation period exhibited normal behavior. We do not have an explanation for the apparent discrepancies of these results.

The observed loss in capacity of the cadmium electrode (in Run #5) indicates a deactivation somewhat more than the excess capacity (about 20%) originally in the electrode. This capacity was permanently lost since recharging of the electrode did not restore it. The material loss is not sufficient to account for it, nor would the simple oxidation expected in the Cd electrode-oxygen reaction do so since this would not be expected to lead to a permanent loss of capacity.

It is possible that an oxidation of the active cadmium on the cadmium electrode is brought about by peroxide decomposition or reaction with hydroxyl free radicals. Also, it may be that radiolysis of the cadmium hydroxide on the electrode occurs. In either case, the resultant materials

might be no longer active and thus no longer able to take part in the electrode reactions. Also, it is known that on cycling, there is an aging process occurring within the electrode and this process may be accelerated by the gamma irradiation. These would result in a reduced electrode capacity and possibly a small steady decline in electrode potential. Both of these effects were observed.

In addition to the effects indicated above, the radiation or the action of a product of radiolysis may change the reactivity of some electrode component. The presence of this new species may help account for the voltage step observed in the post-run discharge of the irradiated cell in Gamma Run #5. Once reacted, this species would no longer be present, so that subsequent recharge and discharge would proceed in normal fashion.

It should be emphasized that these postulates concerning the origin of the changes in electrode capacity and cell voltage are pure speculation. However, they are suggestive of further investigations which may lead to an understanding of the observed effects.

#### B. DISCUSSION OF GAS EVOLUTION

In the radiolytic decomposition of water a variety of reactions occur to give the species H, OH,  $H_2$  and  $H_2O_2$  (Ref. 5, p. 25). The general theory is that radiation decomposes water to H and OH free radicals. In general the principal mode of reaction of the OH is to form hydrogen peroxide,  $H_2O_2$ , while the hydrogen atoms may react with themselves to form hydrogen gas but, to a great extent, diffuse away and react with the medium. The yields of products in pure water are well established but no data have been reported corresponding to the highly basic solutions of this study. It would be expected, however,

in keeping with the Radical Diffusion model (Ref. 5, p. 26), that, in highly basic solutions, the  $\text{H}_2\text{O}_2$  yield would be at least the usual value of 0.7 molecules/100 ev absorbed and the  $\text{H}_2$  yield would be greatly decreased from the value of 0.45 molecules/100 ev absorbed usually observed in dilute solutions. In fact, the principal mechanism leading to hydrogen gas is likely to be from the combination of hydrogen atoms in the track of a radiation event before they have had an opportunity to come in contact with much of the solution. That this mechanism leads to a low yield is indicated by the fact that the gamma irradiation of aqueous solutions of oxidizing agents has resulted in hydrogen yields of essentially zero. (Ref. 5, p. 99.) The electrodes, in contact with the solutions in this study, are likely to have an effect on product yields but information is not available to predict this effect at this time.

In order to obtain some quantitative check on the gas production in these experiments the amount of oxygen gas produced in Run #10 was calculated. The peroxide yield of 0.75 molecules/100 ev obtained by Veselovsky<sup>4</sup> for 0.3 N NaOH solutions was used because his solutions were most similar to those of this study. The steady state concentration of hydrogen peroxide should be quite low because of decomposition due to radiation and to the electrodes and it is assumed, for this calculation, that essentially all of the hydrogen peroxide decomposes to oxygen gas. Using the above yield, an irradiation time of 111 hours, a dose rate of  $1.5 \times 10^{18}$  ev/cc and a solution volume of 45 cc, then the yield of oxygen is

$$\frac{1}{2} \times \frac{.75 \text{ molecules}}{100 \text{ ev}} \times 1.5 \times 10^{18} \frac{\text{ev}}{\text{cc min}} \times 60 \frac{\text{min}}{\text{hr}} \times 111 \text{ hr} \times$$

$$45 \text{ cc} \times \frac{\text{MW}}{6.02 \times 10^{23} \text{ molecules}} \times \frac{22400 \text{ cc at STP}}{\text{MW}} = 62 \text{ cc at STP.}$$

In Run #10 the pressure change is 2.6 psi for the same temperature before and after irradiation, as shown in Figure 9. In addition, the Cd electrode-oxygen reaction accounts for a decrease in oxygen pressure (initial part of plot in Figure 9) of 0.15 psi/hour. Thus the total pressure change for the 111 hour experiment is  $(111 \times 0.15) + 2.6 = 19.2$  psi. If it is assumed that essentially all of this is due to oxygen gas then, in the 45 cc gas volume of the cell, this pressure change corresponds to a volume of oxygen of  $\frac{19.2}{15} \times 45 = 58$  cc at 1 atm. and 25°C.

The agreement of these calculations is much better than would be expected from the data and the nature of the assumptions involved. However, at least in a qualitative sense, the tentative conclusion might be drawn that the above picture is reasonable for the conditions of this work. One of the recommendations for future work (Section V) is a study of product yields for the radiolysis of 30% KOH solutions. Of particular interest are the yields of hydrogen and of hydrogen peroxide and the modes of decomposition of the latter.

## V. RECOMMENDATIONS

The results to date, including the sloughing phenomenon and the single observation of loss of cell capacity on irradiation of Ni-Cd battery electrodes, are felt to warrant further investigation.

Future work should include an effort to determine (a) whether the cadmium electrode does indeed lose capacity and become the electrode limiting cell capacity, and (b) whether the cell voltage does decrease as a result of continued irradiation. Also, the cause of these effects, including the role of the sloughing and of chemical discharge of the cadmium electrode, should be determined. Voltammetric measurements made periodically during runs would enable one to study in more detail the electrochemical changes occurring.

The phenomenon of the sloughing of material from the electrodes should be studied further to determine the mechanism, the origin and the factors influencing it. To this end, the effects of total dosage and dose rate should be correlated further with the amount and composition of sloughed material. A study of the radiolysis products of 30% KOH in the presence and the absence of the individual electrodes may give some insight to the mechanism of sloughing of material from the electrodes.

More information on battery manufacturing techniques is needed to evaluate if variations in the final product inhibit or promote some of the observed phenomena caused by radiation. Some of these possible variations relate to (a) the method of impregnation of the electrodes with active material, (b) the composition of active material used, particularly that of the nickel electrode, (c) type of binder used and (d) type of separator used. More whole commercial cell irradiations should be performed so that the results

with laboratory cells may be related to the effects observed with cells in actual use.

Other types of rechargeable systems should also be studied to see if they are affected in a similar fashion to the nickel-cadmium system under high radiation fields. The silver-cadmium system, for instance, uses the same cadmium electrode as does the nickel-cadmium system. Both the silver-cadmium and silver-zinc cells have good peroxide decomposition catalysts due to the silver, which may cause an even more serious sloughing problem.

In summary, the results to date indicate the need for a further detailed study of the effect of nuclear radiation on all battery electrodes prior to their use in heavy radiation fields.

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